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Original Research

H_2 sensing properties of modified silicon nanowires

Latefa Baba Ahmed[a], Sabrina Naama[b], Aissa Keffous[b], Abdelkader Hassein-Bey[a], Toufik Hadjersi[b,*]

[a]*Département de physique, Université Saad Dahlab de Blida, route de Soumâa B.P. 270, Blida 09000 Algeria*
[b]*Centre de Recherche en Technologie des Semi-conducteurs pour l'Energétique (CRTSE), 2, Bd. Frantz Fanon, B.P. 140 Alger-7 Merveilles, Alger, Algeria*

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Abstract

It has been found that the silicon nanowires modified with noble metals can be used to fabricate an effective H_2 gas sensor in the present study. The preparation and surface modification of silicon nanowires (SiNWs) were carried out by chemical methods. The morphology of the silicon nanowires unmodified and modified with nanoparticles of platinum, palladium, silver and gold was investigated using scanning electron microscopy (SEM). The chemical composition of the silicon nanowire layers was studied by secondary ion mass spectroscopy (SIMS) and energy dispersive X-ray analysis (EDX). The structures of type metal/SiNWs/p-Si/Al were fabricated. The electrical characterization (*I–V*) was performed in primary vacuum and H_2 at different concentrations. It was found that the metal type used to modify the SiNWs strongly influenced the *I–V* characteristics. The response of these structures toward H_2 gas was studied as a function of the metal type. Finally, the sensing characteristics and performance of the sensors were investigated.

Keywords: Electroless chemical etching; Noble metal; H_2 sensor; Silicon nanowires; Morphology

1. Introduction

Recently, silicon nanowires (SiNWs)—owing to their extraordinary chemical, electrical and optical properties—have attracted considerable attention for the materials scientists [1–4]. The high specific surface area and high chemical activity make them to be an interesting candidate for different applications, especially for gas sensing to environmental monitoring and protection. Indeed, these properties permit SiNWs to effectively react with gases. The adsorption of gas molecules on nanowire surface entails a change in the conductivity, which serves as the basis for molecular gas sensing [5]. Thus, the sensor sensitivity is strongly dependent on the surface area. In addition, SiNW arrays show a low reflectance compared to thin films in a wide spectrum range, allowing the fabrication of solar cells without the use of antireflection coatings. This property makes them more suitable for next generation photovoltaic applications. Recently, a hybrid solar cell model composed of a heterojunction cell and a photoelectrochemical (PEC) cell was fabricated [6]. In this structure, a thin film of double-walled carbon nanotubes forms a heterojunction with the silicon nanowire (SiNW) array which also functions as the transparent counter electrode of the PEC cell. Besides, Schottky junction solar cells assembled by coating graphene films on n-type silicon nanowire (SiNW) arrays were developed [7].

A metal-assisted chemical etching method shows a particular interest for the fabrication of SiNWs-based gas sensor [8]. It is a simple, fast, effective, low cost method compatible with conventional silicon technology, and allows obtaining vertically aligned nanowires on silicon substrate with a high density [9]. Moreover, when these nanowires are modified with noble metals, such as Pt, Pd, Ag and Au the novel performance gas sensors could be provided. This is due to the catalytic property of these materials. This property can be considerably improved when they are present in the form of nanoparticles [10].

*Corresponding author.
E-mail address: hadjersi@yahoo.com (T. Hadjersi).
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It is expected that the performances are different for each modification type. Since the catalytic activity and the work function are different for each type of metal. In addition, the interaction of H_2 molecules with these nanoparticles can change their work function or resistivity. For these reasons this work is focused on the study of the sensing properties to H_2 gas for each modification type.

Nanowires modification by physical and chemical vapor deposition leads to poor penetration of metal nanoparticles into the nanowire layer. For this purpose, a wet process like electroless metal deposition is effective and advantageous. Moreover, this process is simple in operation, reliable and inexpensive [11]. The silicon samples are immerged into metal–salt solutions containing HF, and various kinds of metals can be deposited [12–15].

Up to now, there are a few reports on the molecular sensing property of SiNWs. Indeed, recently a SiNW-based biosensor, consisting of SiNWs decorated with AuNP using SAM of APTES molecules to anchor the AuNPs on the nanowire surface was developed [16]. Also, silver-coated SiNW arrays were prepared for molecular sensing and label-free immunoassay sensing using SERS signals, such as rhodamine 6G (R6G), calcium dipicolinate (CaDPA) and immunoglobulin G (gamIgG) [17,18]. Recently it was demonstrated that the sensor made from porous SiNWs substrate, prepared by metal-assisted chemical etching, shows fast response and excellent reversibility to subparts per million NO concentrations [8]. Ni/SiNWs nanocomposites, prepared by wet chemical etching silicon nanowires (SiNWs) coated with electroless plating nickel, were also used to fabricate humidity sensor [19]. More recently, a novel sensor for the detection of H_2O_2 was fabricated based on H-terminated SiNW arrays elaborated via electroless etching decorated with AgNPs [20].

Hydrogen is considered as a cost effective, clean and pollution free fuel that can be an alternative fuel in the present perspective. The deadly explosive nature in ambient environment of this odorless and colorless gas makes it a very dangerous gas. Therefore, it is of great interest to develop efficient and economically viable hydrogen sensors for the detection of hydrogen leakage into the atmosphere. There are several reports on the development of hydrogen sensors mainly based on porous silicon and metal oxide semiconductors [21–27]. However, for the first type, the porous silicon is elaborated by electrochemical anodization which is a more or less complicated method and not compatible with silicon integration technology. In addition, the porous silicon-based gas sensor has a high series resistance leading to significant power consumption [28]. For the second type, the high operating temperature (sometimes up to several hundred degrees Celsius) is the major limitation [25–27].

In this paper, the preparation of a structure of type Al/SiNWs/Si/Al for H_2 gas sensing was reported. SiNWs were formed by metal-assisted chemical etching and modified with noble metals (Pd, Au, Ag and Pt) using the electroless metal deposition method. The samples were characterized by SIMS (secondary ion mass spectroscopy), SEM (scanning electron Microscopy) and EDX (energy dispersive X-ray). The response of the structures toward hydrogen was measured at room temperature.

2. Experimental

P-type Si (100) wafers with a resistivity of 7.7–8.66 Ω cm were used in this work. The silicon wafers were cut into samples of $10 \times 10\ mm^2$ in size. The samples were first cleaned by ultrasonication in trichloroethylene, acetone and deionized water (5 min each). Then the clean samples were dipped into HF (40%) aqueous solution for 1 min to remove the native silicon oxide layer. An Al thin film of about 0.4 μm was evaporated under vacuum ($\sim 8 \times 10^{-6}$ Torr) through a metallic mask onto the back side. The diameter of the deposited layer was about 6 mm. And then the samples were annealed at 577 °C for 30 min in N_2 ambiance. The SiNW arrays were obtained by chemical etching of the clean sample in 9.65 MHF–0.033 M $AgNO_3$–H_2O aqueous solution at 50 °C for 10 min. The resulting surface was rinsed copiously with deionized water and immersed in an aqueous HNO_3 (70%) solution for 5 min at room temperature to remove the silver nanoparticles and dendrites deposited on the surface during the chemical etching. By using a mask, the silicon nanowires were formed on the front side on an area of $9 \times 9\ mm^2$. The modification of silicon nanowires by Ag, Au, Pd and Pt nanoparticles was carried out by the electroless deposition technique. They were deposited on SiNW arrays by dipping the samples into the following aqueous solutions, respectively:

- $AgNO_3$ (0.01 M)/HF (0.5 M) for 1 min at room temperature.
- $AuCl_3$ (1 mM)/HF (0.15 M) for 10 min at room temperature.
- $PdCl_2$ (1 mM)/HF (0.15 M) for 40 min at room temperature.
- PtO_2 (3 mM)/HF (0.15 M) for 1 h at 50 °C.

In the last two solutions, a few drops of HCl were added to facilitate the dissolution of $PdCl_2$ and PtO_2. The resulting surfaces were rinsed with water and dried under a gentle stream of nitrogen. The front contact was obtained by evaporation of an aluminum thin film on the silicon nanowire layer. The diameter of front contact is about 4 mm. The schematic of the SiNWs gas sensor device is shown in Fig. 1a. For the gas sensing study, the samples were placed inside a chamber with inlet and outlet provisions for the gases. High purity H_2 gas was used for the experiments. To measure and to accurately control the flow rates of the gases throughout the experiments, mass flow meters were used. In order to well assess the structure sensitivity toward H_2 gas, a primary vacuum (2×10^{-2} Torr) in the measurement chamber was performed before injecting H_2. This allows reducing the effect of cross-sensitivity from the oxygen in air and thus the sensing mechanism is simplified. The current–voltage characteristics in the dark were measured using an electrometer Keithley 6485 and a voltage/current source ITECH 6121. The schematic of the gas sensor measurement setup is shown in Fig. 1b. The measurements were performed at room temperature. The Schottky diode parameters were extracted from the forward *I–V* curves.

The morphology was examined by scanning electron microscopy (SEM) using a Philips (XL 30) equipped with an energy dispersive X-ray analysis device (EDX analysis).